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Characterization of β -tricalcium phosphate-clay mineral composite obtained by sintering powder of apatitic calcium phosphate and Montmorillonite

M. Jamil^{1,*}, A. Elouahli¹, H. Khallok^{1,2}, B. El ouatli¹ and Z. Hatim¹

¹Team of Energy, Materials and Environment, Department of Chemistry, Faculty of Sciences, University Chouaib Doukkali, El Jadida, Morocco.

²Environmental and Chemical Engineering, Faculty of Technology, University of Oulu, Oulu, Finland

*Corresponding author: mo.jamil@yahoo.fr

Abstract

Calcium phosphates and clay minerals have taken great attention by researchers for medical applications. Recently, numerous researchers have been developing calcium phosphate/ montmorillonite composites as a synthetic bone graft substitutes. In this study, β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP)/Montmorillonite(MNa) composites were developed by sintering powder at 900°C of apatitic tricalcium phosphate ($\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$, TCPa) and unmodified MNa at various amounts (2, 5, and 10 wt.%). The composites were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR) and thermal analysis (TG / DSC). XRD results show that the sintering of TCPa with and without MNa lead to the formation of a single crystallized β -TCP phase and that the addition of the MNa causes a change in its crystalline lattice. The results of XRD, FT-IR and the structural refinement indicate the insertion of the clay ions in the β -TCP structure. This ionic substitution leads to a decrease in lattice parameters and an increase in index distortion. The low percentages of MNa lead to an increase in crystallite size while the high values (10 wt.%) lead to an opposite effect. The change of the composition leads to the stabilization of the β -TCP phase, and the temperature of the allotropic transformation of β to α -TCP shifts toward the higher temperature.

Keywords: β -tricalcium phosphate; Montmorillonite; Substitution; Biocomposite

1. Introduction

Calcium phosphates (CaPs) based biomaterials are widely applied for the regeneration of bone defects [1-4]. Among them, tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP) has recently received special attention as a bone graft substitute due to its similarity with a mineral fraction of human bone tissue [5]. In addition, β -TCP has excellent biocompatibility and osteoconductivity [6-8]. Despite, its high biodegradability, β -TCP exhibits weak bioactivity which limits their applications [9,10]. In order to improve β -TCP biomaterials' bioactivity, research has been focused on the development of β -TCP substituted with various ions such as Na^+ [11], Mg^{2+} [12-14], SiO_4^{4-} [15,16] and Al^{3+} [17,18]. The nature of these ions is inspired by bone mineral composition. Indeed, biological apatites are non-stoichiometric, and contain several ionic substitutions such as Zn^{2+} , Mg^{2+} , Na^+ , Cl^- , CO_3^{2-} ....[19,20,2]. Is known that small quantities of these elements can play a significant role in overall biological processes [21].

Montmorillonite is one of the most studied clay mineral [22,23]. It's a member of the Smectites family with 2:1 layered structure, two silica tetrahedral sheets sandwiching a central octahedral sheet. The isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer will generate a negative charge, which is balanced by exchangeable alkaline or earth alkaline cations as K^+ , Na^+ , Ca^{2+} naturally occurring between the layers [24]. Na-type montmorillonite (MNa) is widely used in medical and industrial applications as of pharmaceutical excipients and as drug delivery system [23,25,26], due to its attractive properties as high swelling capacity, good cation exchange capacity and high specific surface area [27-29]. MNa clay consists of ions such as silicon, magnesium, aluminum and therefore can be useful for bone tissue engineering studies.

Recently, the combination of calcium phosphates and montmorillonite has taken great attention of the researchers for medical applications. Numerous researchers have been reported to prepare hydroxyapatite/montmorillonite [30,31], or Polymer/montmorillonite/Hydroxyapatite composites [27-29,32]. Pazourková L. et al. [30] have prepared the HAP/montmorillonite nanocomposites by two methods: wet precipitation using mixing and ultrasound treatment and the influence of those methods on the prepared nanocomposites has been investigated. Katti K.S. et al. [27] have prepared, by precipitation

in an aqueous medium, a chitosan/montmorillonite/hydroxyapatite nanocomposite with an improved nanomechanical property, biocompatibility, and a better cell proliferation rate. Amber et al, [32] developed a mineralized HAP in montmorillonite clay galleries modified with 5-aminovaleric acid. It was found that there were interactions between the groups of the amino acid modifier and the apatitic ions.

A study by Hesarak S. et al. [31] found that addition of a little amount of montmorillonite (3.5 wt.%) enhanced the mechanical strength, sintering performance and decreased the dissolution rate of the calcium phosphate ceramics without any significant change in their final composition.

In literature there is only one work in which is reported on Montmorillonite/Mg- β -TCP coatings preparation by nanoemulsion coating method for enhancement the stability of orthodontic miniscrews [33]. It is reported that the addition of nanoclay has dramatically improved the wear resistance and cytocompatibility of Montmorillonite/Mg- β -TCP.

Therefore, the development of new biomaterials associating the calcium phosphate ceramics as β -TCP and montmorillonite-clay can be very interesting for biomedical applications especially for the repair and mineralization of bones and teeth.

Moreover, since to our knowledge there has not been any report on preparation of the β -TCP/MNa composite by a powder sintering method. On the other hand, the interaction between unmodified montmorillonite and calcium phosphate as tricalcium phosphate doesn't been discussed.

The aim of this work was to develop and characterize a β -TCP-MNa composite by sintering of apatitic tricalcium phosphate powder ($\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\text{:TCPa}$) with unmodified Na-montmorillonite at variable amounts. The effect of MNa addition on the β -TCP structure was examined by Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM-EDX) and Thermal Analysis (TG / DSC).

2. Experimental

2.1. Materials

The sodium montmorillonite (Cloisite-Na⁺) was obtained from Southern Clay Products, Inc. The cation exchange capacity (CEC) is 92.6 meq/100g of montmorillonite (MNa). The composition of MNa as follows (wt.%): Na₂O 7.223, MgO 4.133, Al₂O₃ 19.986, SiO₂ 56.851, P₂O₅ 0.022, K₂O 0.442, CaO 0.698, MnO 0.053, TiO 0.368, and Fe₂O₃ 7.936.

CaCO₃ (Skora, analytical grade) and H₃PO₄ (Merck: analytical grade) were used as starting chemical precursors for Ca and P, respectively, for the synthesis.

2.2. Preparation of apatitic tricalcium phosphate powder

Apatitic tricalcium phosphate powder (Ca₉(HPO₄)(PO₄)₅(OH):TCPa) was synthesized by the reaction between the calcium hydroxide and orthophosphoric acid according to the method described by Elouahli et al. [34]. Briefly, the calcium oxide powder, prepared by calcination of CaCO₃, was dispersed in double distilled water. The solution of orthophosphoric acid (1mol/l) was then added rapidly at 22 °C into Ca(OH)₂ suspension (0.5 mol/l) using a vigorous stirring (500T/min). The calcium/phosphor molar ratio of the reagents was fixed at 1.50 ± 0.02 (molar ratio of the stoichiometric tricalcium phosphate). The resulting precipitate was filtered, dried at 60°C/12h, and crushed then sieved to retain grains with sizes less than 125 µm.

2.3. Preparation of β-TCP-MNa ceramics

Preparation of β-TCP-MNa biocomposites were performed from montmorillonite (MNa) and apatitic tricalcium phosphate powder (TCPa). The MNa was added to TCPa powder in different weight concentration (2, 5 and 10 wt. % based on TCPa weight). The resulting mixtures were placed in an agate mortar and ground to obtain homogeneous fine particles. The powders then sintered at 900 °C in a muffle furnace for 3 hours at a rate of 5 °C/min.

MNa-free β-TCP powder has also prepared by sintering TCPa at 900°C for 3 hours.

According to the added quantity (x) of MNa, the samples TCP-xMNa are named as follows: TCP-0MNa, TCP-2MNa, TCP-5MNa, and TCP-10MNa.

2.4. Characterization of powders

Infrared Spectra of powders were recorded on a Fourier Transform Spectrometer (SHIMADZU FTIR-8400S) with a resolution of 4 cm⁻¹ and 20 scans. 1% of the powder samples

were mixed with 99% KBr, and then pressed in a 13 mm die, the range of FTIR-spectrum was taken of 400 to 4000 cm^{-1} .

The formed phases were identified on dried and calcined powder using the X-ray diffraction (diffractometer BRUKER D8 ADVANCED). Copper $K\alpha$ radiation ($\lambda = 1.5406$) produced at 50kV and 20mA scanned the diffraction angles 2θ in the range $5-60^\circ$, using a step size of 0.02° and a step time 30s. Crystallographic identification was accomplished by comparing the experimental XRD patterns to standards compiled by the joint committee on powder diffraction standards (JCPDS), which was card #09-0169 for β -TCP. Structural characterization for the prepared samples was carried out with the FullProf program (WinPLOTR 2017). Calculating the distortion of the PO_4 tetrahedrons can provide an estimation of the structural distortion. The tetrahedral distortion index was obtained from the calculated data using the relation (Eq. (2)):

$$D_{ind} = \frac{\sum_{i=1}^6 (\text{OPO}_i - \text{OPO}_m)^2}{6} \text{Eq. (2)}$$

Where OPO_i denotes the six angles between P and the four O atoms of the phosphate tetrahedron and OPO_m is the average angle (around 109.17°).

The crystallite size of the calcined samples was calculated using the Scherrer formula: $L = 0.9\lambda / \beta \cos\theta$ where λ is the wavelength of the used Cu- $K\alpha$ radiation, β is the full width at the half maximum of the β -TCP line and θ is the diffraction angle. The thermal behavior of as-dried samples was investigated by simultaneous thermogravimetry and differential scanning calorimetry (TG-DTA, NETZSCH STA 409PC/PG), in the condition of heating rate $20^\circ\text{C}/\text{min}$. Microstructural analysis of the samples was performed with Scanning Electron Microscope ((LeicaSterioscan 430).

3. Results and discussion

3.1. FT-IR Analysis

The result of Infrared Spectrometry (Fig.1) shows that the prepared powder is apatitic tricalcium phosphate ($\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$: TCPa) which was identified by the vibration bands of PO_4^{3-} groups: $\nu_2 \text{PO}_4$ (474 cm^{-1}), $\nu_4 \text{PO}_4$ ($571-601 \text{ cm}^{-1}$), $\nu_1 \text{PO}_4$ (962 cm^{-1}) and $\nu_3 \text{PO}_4$ ($1026-1107 \text{ cm}^{-1}$). The band at 875 cm^{-1} is assigned to HPO_4 groups. The bands at 630 and 3560 cm^{-1} are characteristic of O-H bond. The bands at 3460 and 1636 cm^{-1} are assigned to H-O-H symmetric stretching and bending vibration.

The spectra of MNa show the bands at 3628, 916 cm^{-1} (O–H stretching), 3443, 1636 cm^{-1} (H–O–H stretching and bending vibration of interlayer in MNa), 1114, 1046 cm^{-1} (Si–O stretching), 891, 849 cm^{-1} (Al–FeOH and Al–MgOH deformation), 798 cm^{-1} (Fe^{3+} –MgOH stretching), 624 cm^{-1} (Coupled Al–O and Si–O vibration) and 523, 465 cm^{-1} (Al–O and Si–OSi deformation).

Fig.1: Infrared spectrum of TCPa precursor and MNa clay

The FT-IR results (Fig.2) shows that the calcination of the TCPa to 900 °C leads to the formation of β -TCP phase. Indeed, the IR spectrum shows several absorption bands including those with 552, 594, 606, 945.972, 1025, 1042, 1120 cm^{-1} that are attributed to the vibration of PO_4 groups in the β -TCP structure.

These same bands were observed in the IR spectrums of the samples: TCP-2MNa, TCP-5MNa, and TCP-10MNa. In addition, we can see the appearance of a new band at 890 cm^{-1} attributed to SiO_4 group whose intensity increases with the increase in the amount of MNa.

Fig.2: Infrared spectrum of: a) TCP-0MNa, b) TCP-2MNa, c) TCP-5MNa and d) TCP-10MNa.

3.2. Structural analysis

The X-ray diffraction pattern of precursor TCPa and the MNa clay are illustrated in Fig.3. For TCPa, the powder exhibited a single apatitic phase without any secondary phase. XRD pattern of MNa showed pure montmorillonite characterized by the 001 reflections situated towards $2\theta = 6.18^\circ$ corresponding to the lattice distance $d_{001} = 14.27\text{\AA}$. XRD analyses samples presented also the characteristic reflections situated towards 2θ 19.76°, 28.69° and 34.75° corresponding to d values of 4.48 $\text{\AA}$ (100), 3.10 $\text{\AA}$ (005) and 2.57 $\text{\AA}$ (110). The width of the peaks indicates that the material is not perfectly crystalline.

Fig.3: XRD patterns of TCPa precursor powder and MNa clay

Fig.4 shows the XRD patterns of the **samples TCP_a with and without MNa**. The result (Fig. 4a) shows that MNa-free TCPa has transformed to pure β -TCP phase (ICDD PDF card 09–0169) **according to the following reaction:**

The XRD patterns (Fig. 4 b-c-d) of the all samples with montmorillonite reveal the presence of the only β -TCP phase and no peak indicating the presence of the secondary phases (α -tricalcium phosphate, hydroxyapatite or other silicate phases). On the other hand, a small shift in peak positions was observed for TCP-xMNa, to the lower 2θ for x=2 and x=5 and to the higher 2θ for x=10 with respect to pure β -TCP (Fig. 5).

Fig.4: XRD patterns of: a) TCP-0MNa, b) TCP-2MNa, c) TCP-5MNa and d) TCP-10MNa.

Fig.5: XRD patterns of: a) TCP-0MNa, b) TCP-2MNa, c) TCP-5MNa and d) TCP-10MNa with the 2θ range of 25 to 30°.

Rietveld refinement of the XRD patterns was performed to give more detailed information about the influence of the clay phase on the β -TCP structure. Fig.6, reflects the quality of fit obtained from refinement, as reflected by trivial differences between calculated and observed for TCP-0MNa and TCP-5MNa.

Fig.6: Refined diffraction patterns of TCP-0MNa and TCP-5MNa (---- experimental — calculated).

The crystallographic characteristics of the prepared samples are reported in Table-1. For the β -TCP prepared without MNa, the crystallographic parameters and the cell volume of β -TCP remain lower than the theoretical values. This result can be due to the insertion of the trace ions coming for example from the raw material.

The results (Fig. 7) of the refinement show that the lattice parameter (a) and the cell volume decreased with increasing of MNa clay amount. The parameter (c) decreases with low percentages of MNa, and increases slightly with higher values (10wt.%) of MNa. The crystal size of the TCP-xMNa samples was also affected. The low percentages of MNa lead to an increase in crystallite size while the high values (10wt.%) lead to an opposite effect. The structural modifications observed are accompanied by a distortion of the crystal lattice of the TCP phase (Table 1). The added MNa increases the index distortion.

These results highlight the change in the TCP structure by incorporation of clay ions.

Table-1: Crystallographic characteristics of TCP-xMNa(x=0, 2, 5 and 10 wt.%) samples.

Fig.7: Evolution a) of parameters (a - c) and b) the cell volume of β -TCP with the concentrations of added MNa.

3.3 Microstructural analysis

SEM images (Fig. 8) show the effect of MNa addition on the microstructure of TCP-10MNa composite. The images show that the samples prepared with and without MNa present a different arrangement of aggregates. For TCP-0MNa (Fig.8a) we can observe a microstructure in separate aggregates with irregular size. SEM-EDX analysis indicates the presence of Ca, P and O, characteristic of the β -TCP phase. In the case of biocomposite TCP-10MNa, a relatively compact microstructure is observed where the aggregates are not well individualized (Fig.8b). The results of SEM-EDX analysis indicate the presence of major elements (Ca, P) and clay ions of Si and Al with Mg and Na as trace ions.

Fig. 8: SEM images and EDX analysis of the samples (a) TCP-0MNa and (b) β -TCP-10MNa

3.3. thermal analysis TG/DSC

The curves of the thermal analysis TG/DSC of the MNa clay are presented in Fig.9. The examination of the thermal analysis curves showed in the low-temperature range, the existence of an endothermic peak located around 100 °C, coupled with a loss of mass of 7.42% of the initial mass, is attributed to the loss of physisorbed water on the external surface. Another endothermic phenomenon occurs at a temperature of 691°C, corresponds to a dehydroxylation characteristic of MNa. The percentage of the loss of mass due to this elimination is of the order of 3.58% by weight. The portion of the curve above 1051°C reflects the modification of montmorillonite structure and formation of crystalline phases as quartz, cristobalite, spinel, mullite, and cordierite [35]. It, therefore, appears that up to 1000 °C, the clay continues to dehydroxylate while maintaining its structure.

Fig.9: Thermal analysis TG/DSC of the MNa clay

Thermal analysis curves DSC/TG of TCP-0MNa and TCP-10MNa powders are shown in Fig.10. The mass loss and thermal effects associated in the field of temperatures below 300 °C are mainly the consequence of the departure of the absorbed water (3.21% and 2.92%, respectively for TCP-0MNa and TCP-10MNa). Between 300°C and 700°C, part of the weight loss is due to the condensation of hydrogenophosphate ions to pyrophosphate ions which precede the decomposition of the apatite. The reactions involved during the transformation of TCPa to β -TCP are as follows reaction [36,37]:

At 750 °C and 757°C, respectively for TCP-OMNa and TCP-10MNa, the mass loss (0.78% and 0.64%, respectively for TCP-OMNa and TCP-10MNa) an endothermic peak associated corresponds to a second reaction involving the transformation of the pyrophosphates ions $\text{P}_2\text{O}_7^{4-}$ to the β -TCP according to the following reaction [37-38]:

The endothermic peak at 1167 °C and 1227°, respectively for TCP-OMNa and TCP-10MNa, are associated with the allotropic transformation $\beta \rightarrow \alpha$ tricalcium phosphate. Indeed, according to Destainville et al. the transformation of the β -TCP in α -TCP occurs at 1150 °C [38]. In the works of Abida et al. [37], this transformation took place towards 1167 °C. Ryu et al. [39] have shown that the β -TCP is transformed to α -TCP phase when treated above 1200 °C.

Fig.10: Thermal analysis TG/DSC of the samples TCP-OMNa and TCP-10MNa

3.4. Discussion

In the present study, we prepared β -TCP-MNa composites by sintering powder at 900°C of TCPa and MNa with variable amounts (0, 2, 5, and 10wt.%). The results of FT-IR and XRD analysis show that the sintering powder at 900°C of TCPa in the absence of the MNa leads to the formation of a single crystallized β -TCP phase and absence of other phases such as hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) or calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) [37,38].

The infrared spectra of the samples TCP with MNa (TCP-xMNa) show also the characteristic bands of PO_4 groups of the β -TCP structure and absence of other phases such as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, $\text{Ca}_2\text{P}_2\text{O}_7$ or α -TCP. In addition, the band which appears at 890cm^{-1} is

assigned to SiO_4 tetrahedral stretching [40, 41]. Its intensity increases with increasing the amount of MNa. Also, we observed a decrease of PO_4 band intensity at 464cm^{-1} . These results indicate that there are substitutions of PO_4 group in the structure of β -TCP by clay ions such as SiO_4 ions. The XRD results show that the TCP-2MNa, TCP-5MNa and TCP-10MNa composed of single β -TCP phase suggest that no thermal decomposition has occurred at 900°C . These results show that the added montmorillonite did not affect the final phase of composites. However, the slight shifts of diffraction peaks position in the range of 25 to 35 2θ , confirmed the substitution of clay ions in the TCP structure. The diffraction peak shift may be due to the decrease of unit cell volume accompanying the presence of MNa. Indeed, the results of the structural refinement show that there is a slight decrease in the crystallographic parameters and the volume of the β -TCP phase in the presence of MNa. This structural change leads to a distortion of the crystalline lattice which increases with increasing concentration of MNa. The results also show that the particles size decreased after addition of 10MNa. These changes confirm the FT-IR and XRD results which show the insertion of clay ions in the β -TCP structure.

In the literature, many works have well-documented the behavior of single or coupled ion substitution in the TCP lattice. The ions incorporation can induce subtle changes in the resultant crystallographic parameters depending upon its concentration and nature of the additives, and the most critical is the size of ion. As reported in the literature [13], smaller ionic radius of Mg^{2+} (0.065nm) than Ca^{2+} (0.099nm), generally favored decrease of the crystallite size and lattice parameters. On the other hand, the crystallite size increased with the substitution of Ca^{++} with Na^+ ions [42].

In this study, the lattice parameters and the particle size of the β -TCP powder prepared using TCPa and MNa were influenced by the multi-substitution of clay ions as Si, Al, Mg and Na. The low percentages of MNa lead to an increase in crystallite size. In accordance with the literature the particle size of the β -TCP powder increased with the substitution of Ca ions with Na ions brought by the clay ions. In contrast, the addition of 10MNa to calcium apatite is associated with an increase in the Mg ions content. In this case, the substitution of Ca ions with Mg ions into the β -TCP structure causes deformation of crystals resulting into reduction of particle size of the ceramics powders.

Recently studies [17,18] have reported that the incorporation of Al^{3+} in TCP structure shows a contraction in the lattice parameters a and c . The contraction in the lattice data is due to the lower ionic radii of Al^{3+} (0.054nm) compared to Ca^{2+} (0.099nm). Yoshida et al. [43] have also reported that the a -axis parameter increases linearly in K-doped β -TCP, while it does not change significantly for Na-doped β -TCP and the c -axis parameter decreases linearly for both substitutions. Most existing reports have investigated the effect of a single or a couple of substitutions on the TCP structure, and their effect can be understood. However, the incorporation of multi ions in the TCP structure is more complex and has not been reported before. In the present study the apparition of the Si–O band in the FTIR spectra, the changes in the crystallite size, in crystallographic parameters, in the distortion index and the positional shifts of the diffraction peaks in the XRD patterns with addition of MNa indicate clearly the incorporation of clay ions in the β -TCP structure.

The results of the thermal analysis showed that MNa is stable at 900°C, and their decomposition is produced at 1050 °C. Moreover, no decomposition occurs in TCP-MNa ceramics at 900°C. The added montmorillonite did not affect the final phase of ceramics and confirms the XRD results. On the other hand, the temperature of allotropic transformation β to α tricalcium phosphate of TCP-MNa shifts toward the higher temperature range (A shift of about 60 °C), which confirms the enhancement of thermal stability of β -TCP-MNa ceramics. A similar phenomenon has been observed by other studies [44,45].

It is known that the relative stability of the α - and β -TCP is highly affected by the presence of some ions [46]. Indeed, it has been reported that the Mg^{2+} stabilizes the β -TCP polymorph [13,15, 47], while the Silicon stabilizes the α -TCP polymorph. In our work, due to addition of MNa-clay, the β -TCP is the stabilized phase. Indeed, during the sintering of TCPa in the presence of a clay phase, the dehydroxylation of MNa and the transformation of TCPa to β -TCP are observed. The thermal reaction between TCP and MNa leads to the formation of β -TCP substituted by clay ions as Si, Al, Mg and Na. The change of the composition leads to the thermal stabilization of the β -TCP phase. We specify that the incorporation of clay ions in the calcium phosphate ceramics has not been discussed in the literature. But we can say that the change of the composition of β -TCP, due to addition of MNa-clay, can be useful to influence the biological and mechanical properties of the prepared composites. Numerous works of literature have reported that the addition of MNa improved biocompatibility, and a better

cell proliferation rate of biocomposite Hydroxyapatite/MNa [27]. Nanoclay showed also the good cytocompatibility of β -TCP/nanoclay coatings [33]. In vivo releasing of calcium, and clay ions as silicon, and magnesium are closely related to the biomineralization processes such as cell adhesion, mineral nucleation, bone metabolism, and resorption.

On the other hand, numerous works of literature reported that the use of montmorillonite improve the mechanical properties of the calcium phosphate blocks and foams [31,48]. Also, we have reported in previous work [49] that the hydroxyapatite parts made with montmorillonite showed an appropriate mechanical stability of the sintered parts compared to those prepared without montmorillonite. The addition of clay generally promotes the densification of materials. This remains in agreement with the compact microstructure of prepared biocomposites observed by SEM.

4. Conclusion

In this study, β -tricalcium phosphate/montmorillonite biocomposites were prepared by sintering powder at 900°C of apatitic tricalcium phosphate in the presence of Na-montmorillonite. The addition of the clay with concentration from 2 to 10wt.% did not affect the final β -TCP phase. During calcinations, dehydroxylation of MNa and transformations of TCPa to β -TCP are observed. The thermal reaction between TCP and MNa leads to the formation of β -TCP substituted by clay ions, which affected the crystallographic parameters, the lattice distortion index and crystallite size. The ionic substitution stabilizes the β -TCP phase and the temperature of allotropic transformation of β to α -TCP shifts toward the higher temperature. The composition of the prepared biocomposites can give them interesting biological applications.

Conflict of interest

The authors declare no conflict of interest

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Fig.1: Infrared spectrum of TCPa precursor and MNa clay

Fig.2: Infrared spectrum of: a) TCP-OMNa, b) TCP-2MNa, c) TCP-5MNa and d) TCP-10MNa.

Fig.3: XRD patterns of TCPa precursor powder and MNa clay

Fig.4:XRD patterns of: a) TCP-0MNa, b) TCP-2MNa, c) TCP-5MNa and d) TCP-10MNa.

Fig.5:XRD patterns of: a) TCP-0MNa, b) TCP-2MNa, c) TCP-5MNa and d) TCP-10MNa with the 2θ range of 25 to 30°.

Fig. 6: Refined diffraction patterns of TCP-0MNa and TCP-5MNa
(---- experimental — calculated).

Fig. 7: Evolution a) of parameters (*a* - *c*) and b) the cell volume of β -TCP with the concentrations of added MNa.

Fig. 8 : SEM images for the samples (a)TCP-0MNa and (b)TCP-10MNa

Fig. 9: Thermal analysis of the MNa clay

Fig. 10: Thermal analysis of the TCP-0MNa and TCP-10MNa

Table-1: Crystallographic characteristics of TCP-xMNa (x=0, 2, 5 and 10%) samples.

Sample	Lattice parameters (Å)		V(Å ³)	D _{ind}	Crystallite Size (nm)
	a=b-axis	c-axis			
TCP _{the}	10.4352	37.4029	3527.28	8	-
TCP-0MNa	10.4128	37.3645	3508.5608	25.26	81.7209
TCP-2MNa	10.4125	37.3504	3507.0005	32.67	126.4720
TCP-5MNa	10.4037	37.3565	3501.6477	35.69	113.3416
TCP-10MNa	10.3934	37.3658	3495.5815	20.62	97.1989